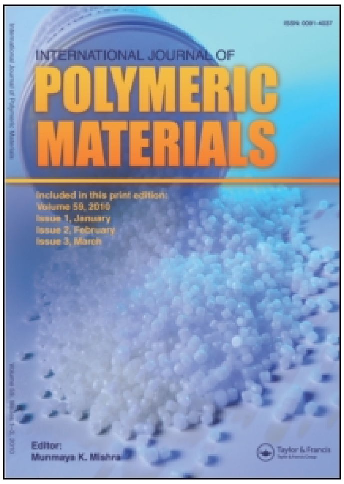

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Kinetics and Mechanism of 2,6-Di-tert-butylhydroquinone Oxidation in Solution

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The kinetics of 2,6-di-tert-butylhydroquinone oxidation was investigated both with spectrophotometry and manometric methods. Kinetic scheme of this compound oxidation with key reaction – interaction of phenoxy radical with oxygen – is suggested.

Keywords: 2,6-di-tert-butylhydroquinone; oxidation; kinetics

AIMS AND BACKGROUND

Problem of hindered phenols oxidation mechanism is arousing interest of investigators during many years. Mechanism of phenol oxidation with different oxidative agents and in polar media was investigated in details [1]. Direct oxidation with oxygen is far less investigated, but supposition about significant role of this reaction for example in the with phenols inhibited polymer oxidation process was made rather long ago [2]. In one of our previously published works it was shown experimentally, that oxidation of phenolic inhibitors occurs with significant rate both in the solution and in the solid polypropylene at 130°C [3], but mechanism of this process is not clarify until now. It is apparently however, that direct reaction of phenol with oxygen is absolutely disadvantageous from standpoint of thermodynamics and

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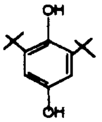
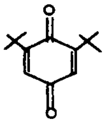
can play significant role only at rather high temperatures [4]. Therefore, mechanism of this process is complex and most probable oxidation of phenol goes on with participation of phenoxy radicals. Investigation of possible mechanism of phenol oxidation was the main purpose of present work.

Direct manometric study of process is not possible even with very sensitive capillary manometric gauge, because even for such model phenols as 2,4,6-tri-tert-butyl- or 4-methyl-2,6,-di-tert-butylphenols oxygen consumption rate is too low. Therefore as a model compound 2,6-di-tert-butylhydroquinone (1) was chosen which oxidability is higher, than for similar phenols. This choice was also a result of fact that it was very convenient to follow the kinetics of hydroquinone comsumption spectrophotometrically, because corresponding quinone (2) was practically single transformation product at least at not very high conversions. Results of spectrophotometric and manometric investigations of hydroquinone oxidation process and some conclusions made on the basis of these data are given in present paper.



(1)



(2)

EXPERIMENTAL

Solvents – heptane and chlorobenzene of special purity grade were used without further purification. Cumene purification method was described earlier [5]. Initiator – azo-bis-isobutyronitrile (AIBN) was purified by recrystallization from heptane and ethanol. Hydroquinone was synthesised and thoroughly purified with sublimation in vacuo and recrystallisation in the Laboratory of stabilisers synthesis of the Institute of Chemical Physics RAS. In the spectrophotometric experiments heptane was used as solvent; to avoid diffusion limitations oxidation experiments were carried out on constant bubbling of air or oxygen. In some experiments for bubbling inert gasses – nitrogen or argon were used, it was necessary for clarification of oxidation processes role in the total kinetics of hydroquinone consumption. As initiator AIBN was used, initiation rates values were from $1{,}7 \times 10^{-8}$ to $4{,}2 \times 10^{-7}$ mole/l.sec. To obtain different initiation rates different concentrations of AIBN (2×10^{-3}–3×10^{-2} mole/l) and different temperatures (55–65°C) were used. At lower temperatures solubility of reagents was pure and at higher – evaporation of heptane became significant.

Absorption spectrum were measured after dilution with the same solvent using Specord UV-VIS spectrophotometer.

For measurements of hydroquinone and quinone concentrations absorption peaks at $\lambda = 289$ nm with $\varepsilon = 4{,}0 \times 10^3$ l/mole.cm and at $\lambda = 254$ nm with $\varepsilon = 1{,}58 \times 10^4$ l/mole.cm correspondingly were used. Even at the more than 50% of initial hydroquinone into quinone conversion two isobestic points were observed in the absorption spectrum, that is to say, that quinone was the only transformation product in these conditions. To avoid possible mistakes connected with superposition of absorption peaks of the both substances for calculations special formulas were used, which were derived as a result of model mixtures with different quinone/hydroquinone proportions investigation. Spectrophotometric data were used for calculations of initial rates of hydroquinone to quinone transformation.

For manometric measurements high-sensitive capillary gauge of Varburg manometer type was used. Solutions of hydroquinone in chlorobenzene were oxidised. Oxidation processes were carry out in the initiated with AIBN regime in the air or oxygen during constant stirring.

RESULTS AND DISCUSSION

On the Figure 1 dependence of hydroquinone consumption (oxidation) rate on the initiation rate is given. Quinone accumulation rates in all cases were the same as the rates of hydroquinone consumption. In the absence of oxygen rate of quinone accumulation was less than 10% of the rate measured in the air. Without initiator hydroquinone autoxidation rate was $1{,}8 \times 10^{-8}$ mole/l.sec (air), in the absence of both of initiator and oxygen hydroquinone concentrations were constant at all studied temperature. Substitution of air with pure

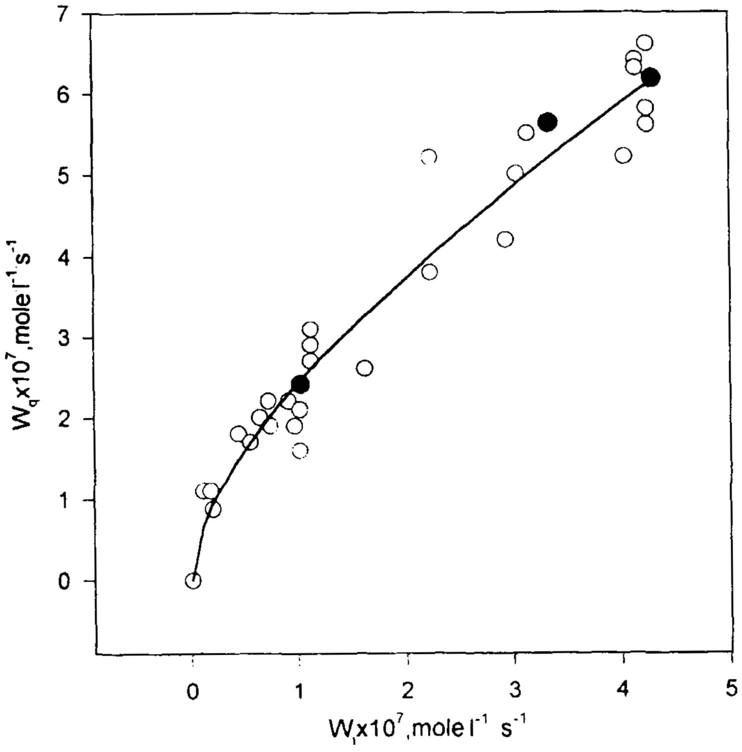


FIGURE 1 Dependence of quinone accumulation (hydroquinone oxidation) rate on the rate of initiation. White points – results of spectrophotometric experiments, black points – results of manometric experiments. Curve is a result of data processing with Sigma Plot computer program, curve parameters are given in the text.

oxygen led to 2,8 times raising – from $2{,}0 \times 10^{-8}$ to $5{,}5 \times 10^{-7}$ mole/l.sec at 55,3°C and initiation rate $6{,}2 \times 10^{-8}$ mole/l.sec.

For obtained data processing following reactions scheme was used.

$$
\begin{array}{llclcl}
 & r\cdot & + & O_2 & \rightarrow & rO_2\cdot \\
k'_7 & PhOH & + & rO_2\cdot & \rightarrow & PhO\cdot + rOOH \\
k_2 & PhO\cdot & + & O_2 & \rightarrow & HO_2\cdot + Q \\
k'_8 & PhO\cdot & + & rO_2\cdot & \rightarrow & rOOH + Q \\
k_9 & PhO\cdot & + & PhO\cdot & \rightarrow & PhOH + Q \\
k_7 & HO_2\cdot & + & PhOH & \rightarrow & H_2O_2 + PhO\cdot \\
k_8 & HO_2\cdot & + & PhO\cdot & \rightarrow & H_2O_2 + Q
\end{array}
$$

In this scheme r is a radical of initiator, PhOH – hydroquinone, Q – quinone. In addition to generally accepted reaction of phenoxy radical with oxygen is introduced. Possibility of such process was demonstrated earlier. Reactions of heptane radicals can be omitted as was showed by comparison of the rates of HO_2 radicals reactions with solvent and with substrate corresspondingly. For mathematical analysis of this kinetic scheme following parameters: W_i, k_7/k_8, k_9 and $k_2[O_2]$ were used. Obtained as a result of calculations complex expression for oxidation rate (quinone accumulation) can be simplified with regard to the fact, that at the quinone concentration, higher than 10^{-3} mole/kg term $k_2[O_2][PhO\cdot]$ can be ignored in comparison with $k_2[O_2](k'_7/k'_8)[PhOH]$. Resulting quadratic equation can be solved regarding PhOH and corresponding solution for rate of quinone accumulation is:

$$W_{Q_{exp}} = A\sqrt{W_i} + BW_i$$

$$\text{where} \quad A = \frac{k_2}{\sqrt{k_9}} \times [O_2] \times \left(1 + \frac{2K_2O_2}{k_9\frac{k_7}{k_8}\text{PhOH}}\right)^{-0,5}$$

$$\text{and} \quad B = 0,5.$$

Plotting of obtained data in the co-ordinates of Eq. (1) permits to obtain experimental values of A and B parameters.

$$A = (6,23 \pm 0,8) \times 10^4 (\text{mole/l.s})^{0,5}$$

$$B = 0,4914 \pm 0,1443.$$

Good coincidence of experimental B value with theory confirms validity of proposed scheme.

With use of approximate values of the rate constants it is possible to obtain values of the $k_2[O_2]$ parameter in the air and in the oxygen. Calculations were made for initiation rate 10^{-7} mole/l.sec. If $k_7/k_8 = k'_7/k'_8 = 10^{-3}$ and $k_9 = 6 \times 10^6$ l/mole.sec[7], this parameter for air atmosphere is 2 sec^{-1} and for oxygen 9,56 sec^{-1}. For $k_7/k_8 = 5 \times 10^{-4}$, $k'_7/k'_8 = 5 \times 10^{-3}$ and $k_9 = 6 \times 10^6$ l/mole.sec corresponding parameter values are 1,65 sec^{-1} and 7,88 sec^{-1}. This data can be used for the evaluation of consumption rate in the reaction of phenoxy radicals oxidation.

Calculated for the first of these two cases dependence of phenoxy radical concentration on the concentration of phenol is given in the Figure 2. Limit values of phenoxy radicals concentrations towards which the curves asymptotically approach, are determined with equation:

$$[\mathrm{PhO}\cdot] = \sqrt{\frac{W_i}{k_9}}$$

and their values are $1{,}291 \times 10^{-7}$ mole/l for the first case and $1{,}2127 \times 10^{-7}$ mole/l for the second one.

For example, at the phenol concentration 3×10^{-3} mole/l phenoxy radicals concentrations are 7,77 and $10{,}65 \times 10^{-8}$ mole/l and phenoxy radicals oxidation rates are $1{,}76 \times 10^{-7}$ (air) and $6{,}12 \times 10^{-7}$ mole/l.sec (oxygen). This value differs from oxidation consumption rate by $2W_i$ – rate of oxidation of radicals, formed in the initiation act; at sufficiently high phenol concentrations this value can be neglected.

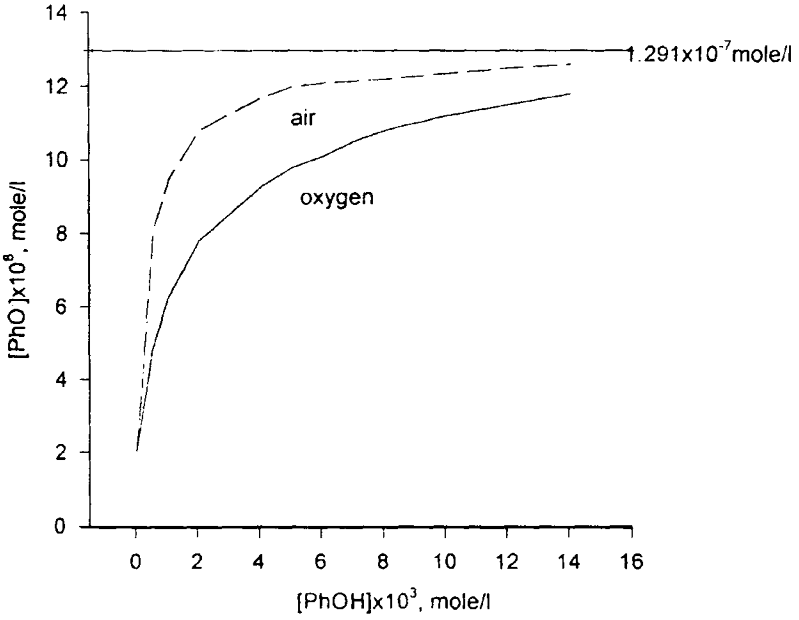


FIGURE 2 Dependence of calculated phenoxy radicals concentration in the air and in the oxygen on the concentration of hydroquinone.

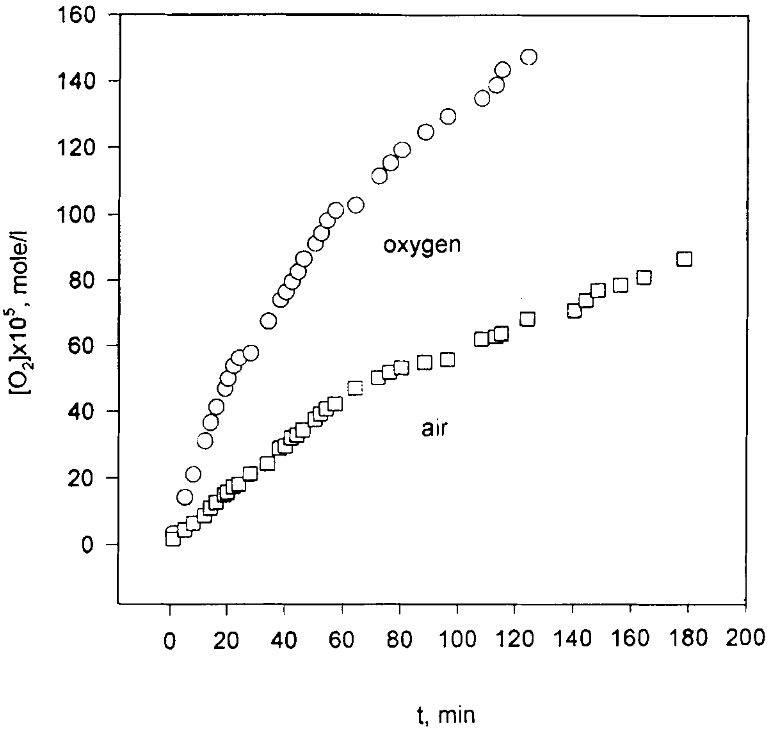


FIGURE 3 Kinetic curves of oxygen consumption in the processes of hydroquinone initiated oxidation in the air and oxygen (60°C, hydroquinone concentration – $3{,}1 \cdot 10^{-3}$ mole/l, $W_i = 1{,}1 \cdot 10^{-7}$ mole.l/s).

Momentary stoichiometric coefficient of inhibition is given with expression:

$$n = \frac{W_i}{(d\,\mathrm{PhOH}/dt)}$$

and in the under investigation system in the range of initiation rates from 10^{-8} to 4.2×10^{-7} mole/l.sec has to change from 0,15 to 0,68.

Value of stoichiometric coefficient of inhibition for the oxidation process inhibited with hydroquinone has to reduce during transition from air to oxygen. This fact was checked experimentally. Indeed for the process of cumene oxidation value of n decreased from 0,71 to 0,34 when instead of oxygen air was used in manometric experiments (cumene-chlorobenzene 4:1, initiator AIBN, initiation rate $1{,}25 \times 10^{-7}$ mole/l.s, 60°C).

Manometric measurements of oxygen consumption rates by the solutions of hydroquinone in chlorobenzene with AIBN initiation in the air and oxygen were made (because of its low boiling point heptane could not be used). In the Figure 3 typical kinetic curves of initiated hydroquinone oxidation in the oxygen atmosphere and in the air are shown. Initial rate in the oxygen is 2,8 times higher, than in the air. Deceleration of hydroquinone oxidation rate is a result of its consumption in the course of reaction. Points, corresponding to initial rates of oxidation in these experiments are given in the Figure 1 together with data of the spectrophotometric experiments. Both set of data can be described with the same kinetic law. As was said above oxidation rates differ from quinone accumulation rates by the value $W_i/2$, but this value is small in comparison with initial oxygen absorption rates and can be neglected.

Thus, in accordance with earlier suppositions kinetic scheme with key reaction of phenoxy radical with oxygen can describe both set of experiments. This reaction is one of the processes of unproductive inhibitor consumption and besides it results in additive initiation by active hydroperoxy radical. Taking this reaction into account is necessary for evaluation of phenoxy radicals efficiency in the both polymers and low molecular substances oxidation processes.

Acknowledgements

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